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# Site Disorder Induced Hexagonal–Orthorhombic Transition in $\text{Y}^{3+}_{1-x}\text{Gd}^{3+}_x\text{MnO}_3$

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We show that the transition in  $\text{AMnO}_3$  from the orthorhombic perovskite phase to the hexagonal phase is promoted by inducing site disorder on the A-site. The gap between the orthorhombic and the hexagonal phase is widened for site disordered, mixed yttrium–gadolinium manganite samples. At the cost of the orthorhombic phase, a two phase region emerges. The phase separation exhibits very unusual thermodynamical behavior. We also show that high-pressure synthesis favors the orthorhombic phase.  $\text{YMnO}_3$  is formed in the orthorhombic phase at 15 kbar.

## Introduction

In the search for new composition–properties relations,  $\text{ABO}_3$  compounds have attracted a lot of attention. The perovskite materials,  $\text{ABO}_3$ , have been researched extensively because this structure forms the basis for interesting physical properties such as high  $T_c$  superconductivity<sup>1</sup> and colossal magnetoresistance.<sup>2</sup> Non-perovskite  $\text{AMnO}_3$ , with  $A = \text{Y}, \text{Ho}, \dots, \text{Lu}$ , attracted renewed interest, due to their ferroelectric properties.<sup>3</sup> These hexagonal  $\text{AMnO}_3$ <sup>4</sup> have a basically different structure than most  $\text{ABO}_3$  compounds, which are distorted perovskites. These properties arise because of the strong correlation of the 3d electrons with the O 2p orbitals.

In this paper, we report the transition from the orthorhombic perovskite (o) to the hexagonal (h) phase by changing the ionic radius of the A ion and by high pressure synthesis. The effect of the ionic radius on the transition is studied by partially replacing Y by Gd ions in  $\text{YMnO}_3$ . The resulting phase diagram leads us to discuss the effect of site disorder, in terms of the ionic radius variance, on the stability of the hexagonal and orthorhombic phases.

The basic building block of the perovskite is an oxygen octahedron with a transition metal, B, in its center. The A ions, usually lanthanides or alkaline earth metal ions, occupy the holes between the octahedra, which form a 3D corner shared network. In this picture, B is 6-fold and A is 12-fold coordinated. Most perovskites have a distorted structure, derived from this building block. The distortions have various origins, including a ferroelectric transition for B a  $d^0$  transition metal ion like  $\text{Ti}^{4+}$ .<sup>5</sup> The most common distortion originates from the relative small radius of the A ions compared with the

holes between the octahedra. This results in a cooperative rotation of the octahedra known as the  $\text{GdFeO}_3$  distortion.<sup>6</sup> Although the structure is interesting in its own right, it has also large effects on the physical properties. It is well documented that both the average ionic radius and the size difference, or variance  $\sigma^2$ , control the properties of perovskites.<sup>7–10</sup> An overview on the properties of the manganites is given in refs 11 and 12.

The magnitude of the  $\text{GdFeO}_3$  distortion depends strongly on the tolerance factor,  $t$ :

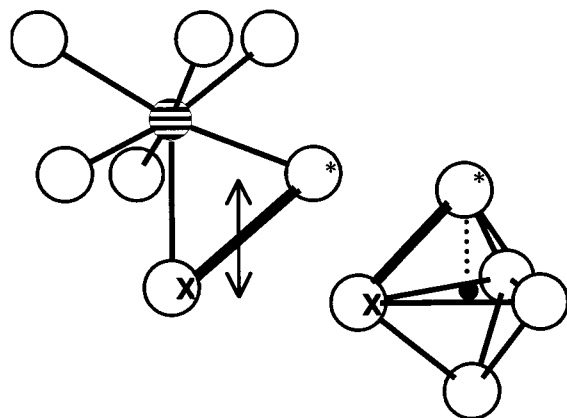
$$t = [r_{\text{A}^{3+}} + r_{\text{O}^{2-}}] / [\sqrt{2}(r_{\text{B}^{3+}} + r_{\text{O}^{2-}})] \quad (1)$$

where  $r_X$  is the radius of the X ion. The tolerance factor gives the relation between the radii of ions A, B, and O in a ideal cubic perovskite. For  $t = 1$ , the size of the lanthanide is exactly right to compose the cubic perovskite system. For  $\text{Mn}^{3+}$ ,  $r_{\text{Mn}^{3+}} = 0.645 \text{ \AA}$  and  $r_{\text{O}^{2-}} = 1.42 \text{ \AA}$ , and this yields a ionic radius  $r_{\text{A}^{3+}} = 1.50 \text{ \AA}$ , where the largest lanthanide, La, has a radius of  $1.22 \text{ \AA}$ . The corresponding tolerance factor  $t = 0.90$  indicates a large distortion for  $\text{LaMnO}_3$ . With increasing atomic number, the lanthanide radius decreases, and thereby, the distortion increases. For the manganites, the tolerance factor is conventionally regarded as the factor controlling the boundary between the hexagonal and orthorhombic structures. The orthorhombic perovskite phase is stable for  $t > 0.855$ , corresponding to  $r_{\text{A}} \geq r_{\text{Dy}}$ .<sup>13</sup> For  $t < 0.855$  and  $r_{\text{A}} \leq r_{\text{Ho}}$ , the hexagonal phase prevails.<sup>4</sup> Yttrium, although not in the lanthanide

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**Figure 1.** Sketch view of the local environment, showing  $AO_7$ , left side, and  $MnO_5$ , right side. The arrow indicates the distance between two oxygen planes. The dashed line indicates the  $Mn-O_{ap}$  distance. Atoms marked with "\*" and with "X" are identical; the thick line indicates the shared edge.

**Table 1. Ionic Radii and Tolerance Factors for Relevant Compounds**

compound	tolerance factor	ionic radius (Å)
$LaMnO_3$	0.902	1.215
$GdMnO_3$	0.866	1.109
$DyMnO_3$	0.857	1.083
$YMnO_3$	0.854	1.075
$LuMnO_3$	0.840	1.032

series, behaves chemically identical, and its radius falls between dysprosium and holmium. An overview on the ionic radii and tolerance factors of some relevant compounds is given in Table 1.

The high-temperature phase of the hexagonal  $AMnO_3$  consists of 8-fold coordinated A ions in bicapped antiprisms. Trigonal bipyramidal holes are formed between two layers of face-sharing antiprisms by the edges of the capping oxygens with the antiprisms. The capping oxygens of two adjacent layers are located on the same  $ab$  plane. Half of the bipyramidal holes are occupied by Mn. The apical oxygens of the  $MnO_5$  bipyramid are also the oxygens that make up the antiprism. The two polyhedra are sketched in Figure 1, where the shared edge is shown. The  $Mn-O_{ap}$  distance is thus equal to the distance between the antiprism oxygen layer and the capping oxygen layer. The steric hindrance of the Mn restricts this layer separation and therefore increases the  $A-O_{ap}$  bond length. Thus, the 8-fold coordination is not uniform. The two apical oxygens have slightly larger bond lengths. Furthermore, the structure is unstable against a ferroelectric distortion at lower temperatures. The apical oxygens move in such a way that one bond becomes "normally" short, whereas the other becomes about 1 Å larger. The asymmetric A environment is the main reason for the ferroelectric behavior. As we have two lanthanide positions in  $P6_3cm$ , we have two nonequivalent, although similar, dipole moments. Four out of the six moments per unit cell point upward; the other two point downward.

Although the hexagonal phase of  $YMnO_3$  at ambient conditions is the thermodynamically stable phase, there are several ways to obtain orthorhombic  $YMnO_3$ . Using thin film growth, an appropriate substrate will force the coherent growth of the orthorhombic phase.<sup>14</sup> Synthesis routes via organic precursors and low reaction temperatures yield the orthorhombic phase.<sup>15</sup> Last, high-

pressure synthesis favors the orthorhombic phase, because it has a higher density.<sup>16</sup>

## Experimental Section

Polycrystalline ceramic samples of  $AMnO_3$ , where A is a mixture of Y and Gd, have been synthesized using regular solid-state synthesis at ambient pressure. Starting materials were  $Y_2O_3$ ,  $Gd_2O_3$ , and  $MnO_2$ . Stoichiometric amounts corresponding to formulas which range from pure  $YMnO_3$  to pure  $GdMnO_3$  were weighted and wet-mixed using acetone as liquid medium. The pressed pellets were sintered for 24 h at 1250 °C and for 24 h at 1400 °C.

High-pressure experiments were carried out both on the mixture of oxides and on as-prepared samples. X-ray powder diffraction patterns were identical for both methods. The high-pressure high-temperature piston cylinder apparatus is a Depth of the Earth Quickpress 3.0, with an experimental range up to 25 kbar and 2100 °C.<sup>17</sup> The lower pressure limit is ~1–2 kbar.

The sample environment is a complex setup, including a graphite furnace and the pressure medium. Care has to be taken to prevent contamination from the graphite resistance furnace or any of the other materials, e.g.,  $Al_2O_3$  or NaCl, in the sample assembly. Therefore, a small amount of powder ~0.5 g was encapsulated in a Pt capsule. The capsule consisted of a tube (diameter 4 mm and height 6 mm) and two preshaped lids, which were welded together using a small welding apparatus. Recovery of the pellet from the sample assembly is improved by the Pt container.

X-ray diffraction patterns were recorded using a Bruker-AXS D8 powder diffractometer, with primary and secondary monochromator, using  $Cu K\alpha_1$  radiation. Patterns were analysed for phase determination using the evaluation software EVA,<sup>18</sup> the Powder Diffraction File,<sup>19</sup> and the Inorganic Crystal Structure Database.<sup>20</sup> Patterns of noncontaminated samples, containing only the hexagonal and orthorhombic phases, were used in the Rietveld refinement using TOPAS R.<sup>21</sup> Rietveld refinements included lattice parameters, zero-point correction, and the ratio between the two phases. Atomic positions were assumed to be constant, because the changes in the atomic positions of  $AFeO_3$  as reported by Marezio et al. are very small. The oxygen and rare earth atomic positions change by 0.005 and 0.004, respectively, when replacing Gd by Ho,  $r_{Ho} \approx r_Y$ .<sup>22</sup> We used the positions as determined by single-crystal X-ray diffraction on  $YMnO_3$ .<sup>23</sup> The ratio Y:Gd was fixed at the nominal composition.

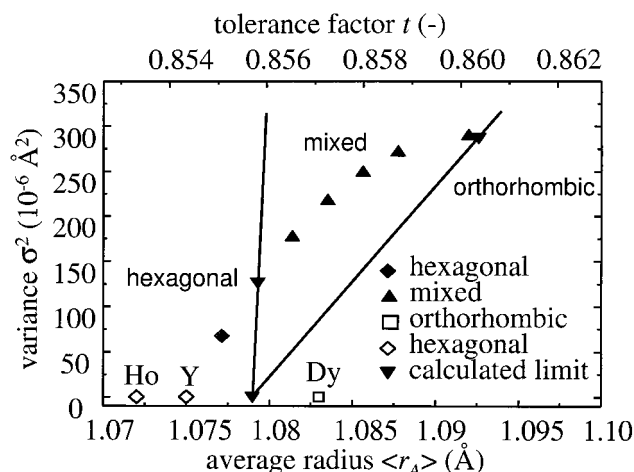
## Results and Discussion

In Figure 2, we present a phase diagram of  $Y_{1-x}Gd_xMnO_3$  as a function of  $r_A$  and its variance  $\sigma^2$  of samples given in Table 2. The variance  $\sigma^2$  is given by

$$\sigma^2 = \sum_1^n x_i (r_i - \langle r_A \rangle)^2 \quad (2)$$

The phase diagram can be divided in three regions. Low

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**Figure 2.** Phase diagram of  $Y_{1-x}Gd_xMnO_3$  as a function of  $r_A$ , or  $t$ , and the variance,  $\sigma^2$ . Diamonds indicate the hexagonal phase, triangles indicate the mixed phase, and squares indicate the orthorhombic phase. The drawn lines are estimates of the phase boundaries as explained in the text.

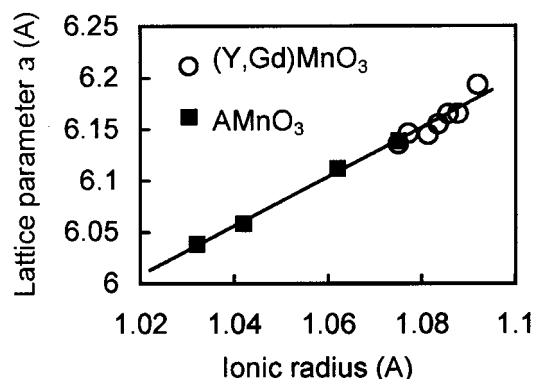
**Table 2. Ionic Radii, Tolerance Factors, and Variance of the Studied  $Y_{1-x}Gd_xMnO_3$  Samples**

$x$	$r_A$ (Å)	$t$	$\sigma^2$ ( $10^{-6}\text{Å}^2$ )
0	1.075	0.854	0
0.06	1.077	0.855	68
0.19	1.081	0.857	176
0.25	1.084	0.857	217
0.31	1.086	0.858	248
0.38	1.088	0.859	271
0.5	1.092	0.860	289
1	1.109	0.866	0

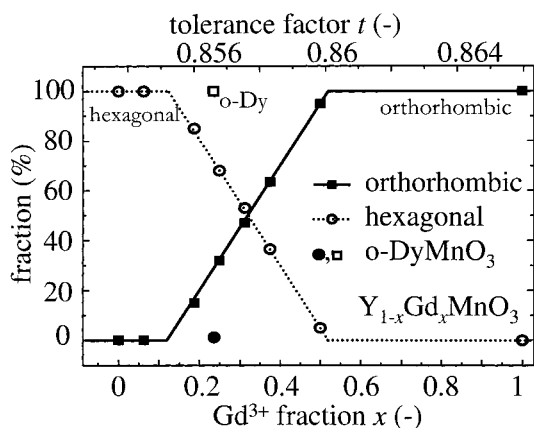
$r_A$  compounds,  $\langle r_A \rangle < 1.078$ , are hexagonal. Large  $r_A$  and small  $\sigma^2$  compounds are orthorhombic. The intermediate region shows both phases. The data for  $HoMnO_3$  and  $DyMnO_3$  have been taken from the literature.<sup>4</sup>

By changing the value of  $x$ , we substitute Y by Gd, whereby  $r_A$  increases linearly. The tolerance factor of orthorhombic  $DyMnO_3$  is equal to that of  $Y_{1-x}Gd_xMnO_3$ , with  $x = 0.23$ . Thus, for  $x \geq 0.23$ , we expect to see the orthorhombic phase. For smaller  $x$  and  $t$ , the hexagonal phase is expected. For  $x = 0$  and 0.06, we indeed found the hexagonal structure. However, for  $0.19 \leq x \leq 0.38$ , we do not observe a sharp transition to the orthorhombic structure but a mixture of the hexagonal and orthorhombic phases. Only for  $x = 0.5$  an (almost) pure orthorhombic compound is found. The anomalous behavior of the mixed Y and Gd samples is best illustrated by focusing on the sample with  $x = 0.25$ , which has an almost identical tolerance factor as  $DyMnO_3$ . Where the latter sample is orthorhombic, the former segregates in both phases. The only difference between the two compounds is that one is undoped and the other has a mixed lanthanide composition.

The lattice parameters of the orthorhombic and hexagonal phases are determined by Rietveld refinement of the powder diffraction data, see Figure 3. We can rule out element segregation of Y and Gd, because the continuous increase in the lattice parameter  $a$  of the hexagonal phase with increasing Gd concentration indicates perfect mixing of the A ions. A linear increase in  $a$  with  $r_A$  is also observed for the single A cation h- $AMnO_3$  series.<sup>4,23,24,25</sup> Figure 4 shows that the orthorhombic phase fraction, as determined by the Rietveld



**Figure 3.** Lattice parameter  $a$  of the hexagonal phase as a function of the Gd content  $x$ . The solid line indicates the linear behavior through the single-crystal data, represented by squares.



**Figure 4.** Relative amounts of hexagonal (circles), and orthorhombic (squares) fractions as a function of the Gd content  $x$ . An open square is plotted for  $DyMnO_3$  at the corresponding value of the tolerance factor.

refinement, increases linearly with the Gd fraction. This allows us to apply the lever rule on the h-o transition

$$\frac{x - x_{\text{hexa}}}{x - x_{\text{ortho}}} = \frac{y_{\text{ortho}}}{y_{\text{hexa}}} \quad (3)$$

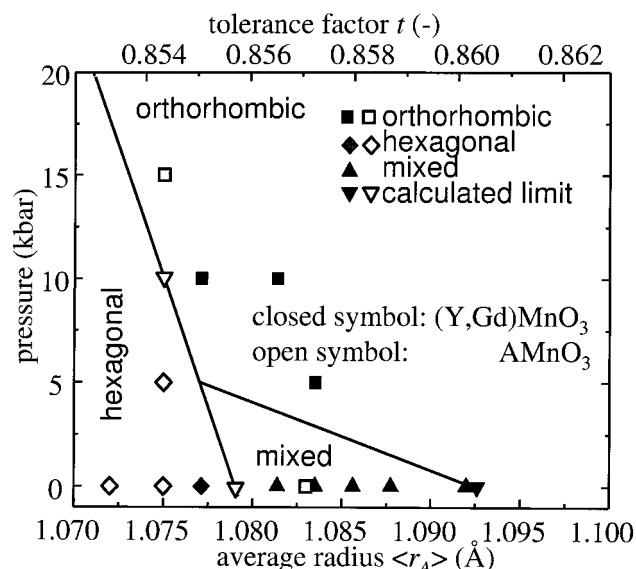
where  $x_{\text{hexa}}$  and  $x_{\text{ortho}}$  are the boundary values for the respective phases and  $y_{\text{ortho}}/y_{\text{hexa}}$  is the ratio of the two fractions. From the observed ratio  $y_{\text{ortho}}/y_{\text{hexa}}$  as a function of  $x$ , the boundary values are derived. The boundary values derived from all five mixed phase samples are plotted in Figure 2 as inverted triangles.

We construct a preliminary phase diagram by assuming that the h-o transition at  $\sigma^2 = 0$  occurs halfway between hexagonal  $YMnO_3$  and orthorhombic  $DyMnO_3$ . The phase boundaries are drawn in Figure 2 as straight lines through the two calculated boundary values and the assumed  $\sigma^2 = 0$  midpoint. This phase diagram can be described as follows. The phase line associated with the upper  $t$  limit of the hexagonal phase does not depend on the variance. Slightly increasing  $\sigma^2$  and  $t$  results in the appearance of a two-phase region, consisting of both the hexagonal and the orthorhombic phase. With in-

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**Figure 5.** Pressure versus average radius phase diagram. Undoped samples are shown with open symbols, and doped Y-Gd samples are shown with closed symbols. We never observed mixed phase samples after high-pressure synthesis. Schematic phase boundaries are drawn.

creasing tolerance factor, the fraction of the orthorhombic phase increases until the lower boundary limit for the orthorhombic phase is crossed. This limit strongly depends on  $\sigma^2$ . The lower limit for the orthorhombic phase increases from  $r_A = 1.078$  Å at  $\sigma^2 = 0$  to  $r_A = 1.093$  Å at  $\sigma^2 = \sigma^2_{\max}$ . Note that  $r_A = 1.093$  Å corresponds with the ionic radius of terbium, the second smallest lanthanide to form the perovskite structure.

We have shown the dependence of the h-o transition on the average radius  $r_A$  and  $\sigma^2$ . In the next section, the effect of high-pressure experiments on the h-o transition will be discussed.

We applied high pressure and high temperature to convert or synthesize some of the conventionally hexagonal samples in the orthorhombic state. Pressure generally stabilizes the most dense phase, in this case, the orthorhombic structure. First, we consider samples with  $\sigma^2 = 0$ .  $YMnO_3$  is still hexagonal at 5 kbar, but the orthorhombic phase is found using a pressure of 15 kbar. The data are shown in Figure 5. The necessary pressure for the h-o transition, less than 15 kbar, is much less than reported previously in the literature.<sup>16</sup> The h-o transition phase line has been sketched in Figure 5 by using midpoints. Extrapolating the pressure dependence of the h-o transition yields a critical pressure of  $\approx 27$  kbar for  $HoMnO_3$ . The error bar on this value,  $\sim 10$  kbar, is large because of the sparse data points.

We also carried out high-pressure experiments on the  $Y_{1-x}Gd_xMnO_3$  compounds. The necessary pressure to induce the orthorhombic phase from the phase mixture decreased with increasing  $r_A$ .

We note the following observations of the two-phase region: (1) The phase mixture is only observed for ambient pressure synthesis for samples with  $\sigma^2 \neq 0$ . (2) We do not observe the mixed phase for any of the experiments at high pressure ( $\geq 5$  kbar). We cannot exclude the presence of the mixed phase at low pressures, but our experimental setup is not well-suited for those pressures. (3) The lattice parameters of both phases in the two phase region indicate no segregation into Y-rich and Gd-rich phases, see Figure 3, which is unconventional. (4) The literature reports that synthesis via organic precursors can result in a mixture of hexagonal and orthorhombic phases for  $AMnO_3$ ,  $\sigma^2 = 0$ , compounds.<sup>15</sup>

These observations lead to the following conclusions. For  $\sigma^2 = 0$  compounds, either the hexagonal or the orthorhombic structure is stable. Whereas low-temperature synthesis may yield mixed phase samples, a high-temperature anneal will convert the unstable phase. The hexagonal or orthorhombic phase will be stable depending on the tolerance factor. However, for  $\sigma^2 \neq 0$ , mixed phase samples can be obtained for a broad range of tolerance factors. Even a high-temperature anneal retains the phase segregated state. Surprisingly, the phase segregation is not accompanied by two limiting compositions, e.g.,  $Y_{1-x}Gd_xMnO_3$  with  $x = 0.1$  and  $0.5$ . The continuous increase of the lattice parameters of both the hexagonal and the orthorhombic phase throughout the two-phase region indicates that the composition of the hexagonal and the orthorhombic state are the same in the mixed state. We have no explanation for this unconventional form of phase segregation.

## Conclusions

We have constructed phase diagrams for the h-o phases of  $AMnO_3$ , including the effects of average ionic radius, hydrostatic pressure, and variance. For compounds with  $\sigma^2 \neq 0$ , a phase separation in the orthorhombic and the hexagonal phase is found. The mixed region exists only at low pressures. We have shown that at ambient pressure, this region expands toward higher values of the average radius with increasing variance. The upper limit for the hexagonal phase is not affected by an increase in the variance. We speculate that disorder, introduced by a large variance or soft chemical synthesis routes, allows the occurrence of the phase separation in the absence of other driving forces. Suppressing the disorder by applying external pressure or annealing at high temperatures prevents the existence of the phase separation. Pressure favors the denser, orthorhombic phase, whereas thermal annealing promotes the hexagonal phase.

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